Evaluation of Soils for Use as Liner Materials: A Soil Chemistry Approach

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ABSTRACT

Movement of NH_4^+ below animal waste lagoons is generally a function of the whole-lagoon seepage rate, soil mineralogy, cations in the lagoon liquor, and selectivity for NH_4^+ on the soil-exchange sites. Binary exchange reactions (Ca^{2+}–K^+, Ca^{2+}–NH_4^+, and K^+–NH_4^+) were conducted on two soils from the Great Plains and with combinations of these soils with bentonite or zeolite added. Binary exchanges were used to predict ternary exchanges (Ca^{2+}–K^+–NH_4^+) following the Rothmund–Kornfeld approach and Gaines–Thomas convention. Potassium and NH_4^+ were preferred over Ca^{2+}, and K^+ was preferred over NH_4^+ in all soils and soils with amendments. Generally, the addition of bentonite did not change cation selectivity over the native soils, whereas the addition of zeolite did. The Rothmund–Kornfeld approach worked well for predicting equivalent fractions of cations on the exchanger phase when only ternary-solution phase compositions were known. Actual swine- and cattle-lagoon solution compositions and the Rothmund–Kornfeld approach were used to project that native soils are predicted to retain 53 and 23%, respectively, of the downward-moving NH_4^+ on their exchange sites. Additions of bentonite or zeolite to soils under swine lagoons may only slightly improve the equivalent fraction of NH_4^+ on the exchange sites. Although additions of bentonite or zeolite may not help increase the NH_4^+ selectivity of a liner material, increases in the overall cation exchange capacity (CEC) of a soil will ultimately decrease the amount of soil needed to adsorb downward-moving NH_4^+.

S OIL-LINED EARTHEN BASINS are often used to store and treat wastes from animal-feeding operations in the Great Plains. These lagoons range in size from 0.5 to 2.5 ha, with a depth of up to 6 m, and generally have compacted soil liners from 0.3 to 0.6 m thick (Ham and DeSutter, 2000). Liners may be constructed using soil present on-site or soil may be brought in from an external source. Bentonite may be added to the liner to reduce hydraulic conductivity. Historically, these soils have only been evaluated on their ability to restrict water movement and, although suggestions have been made that the CEC of the liner material should be included in the liner-evaluation procedure (Barrington and Madramootoo, 1989; Ham and DeSutter, 2000), chemical properties of the liner materials have gone largely unevaluated.

Recent reports have indicated that a substantial amount of NH_4–N can move into the soil underlying animal waste lagoons (DeSutter et al., unpublished data, 2005; Ham and DeSutter, 1999, 2000). Movement of NH_4^+ into the soil is dependent on the whole-lagoon seepage

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rate and the concentration of NH_4^+ in the liquor (Ham and DeSutter, 1999, 2000). Further movement of NH_4^+ into the underlying soil also would be a function of the mineralogy and subsequent CEC of the soil (Barrington and Madramootoo, 1989; Ham and DeSutter, 2000) and the effect of competing cations for exchange sites (Lance, 1972).

Movement of NH_4^+ into the soils underlying lagoons has been investigated by DeSutter et al. (unpublished data, 2005), Ham (2002), Ham and DeSutter (2000), Maule and Fonstad (1996), Miller et al. (1976), Parker et al. (1995), and Perschke and Wright (1998). In most instances, NH_4^+ concentrations were greatest near the lagoon floor and decreased with depth beneath the lagoon. Although most NH_4^+ concentrations decreased with depth, NH_4^+ concentrations were still above expected background levels at the lowermost sampling interval indicating that the true depth of NH_4^+ movement was not reached by sampling (DeSutter et al., unpublished data, 2005; Ham, 2002; Ham and DeSutter, 2000; Miller et al., 1976; Parker et al., 1995; Perschke and Wright, 1998).

Ham and DeSutter (1999) developed an export model to predict the depth of soil (Z_{eq}), in m, needed to adsorb 100% of the downward moving NH_4^+ from animal waste lagoons:

$$Z_{eq} = [NH_4^+]S_t/\rho_b(CEC)(EFA) \qquad [1]$$

where $[NH_4^+]$ is the ammonium charge concentration ($cmol_c\ m^{-3}$) in the lagoon liquor; S_t is the total depth of seepage over the time period of interest (m); ρ_b is the bulk density of the soil ($kg\ m^{-3}$); CEC is the cation exchange capacity of the soil ($cmol_c\ kg^{-1}$); and EFA is the equivalent fraction of NH_4^+ on the soil's exchange sites. Although Ham and DeSutter (2000) used an EFA of 0.87 based on the work of Lance (1972), research suggests that the actual EFA in the upper 0.5 m of cattle and swine lagoons may actually be only as much as 0.22 and 0.44, respectively (DeSutter et al., unpublished data, 2005). The EFA of a soil is a function of the selectivity of the soil for NH_4^+ relative to that of other cations (i.e., Ca^{2+}, Mg^{2+}, K^+, and Na^+) in the waste for exchange sites (Ham, 2002).

The model was used to predict Z_{eq}, in cm, and compare differing scenarios of CEC and EFA when using a constant concentration of NH_4^+ in the waste of 910 mg NH_4–N L^{-1} (6500 $cmol_c\ m^{-3}$), a bulk density of 1400 kg m^{-3}, a seepage rate of 1.1 mm d^{-1}, and a time of one year (Fig. 1). If a soil has an EFA of 0.1 and CEC of 10 $cmol_c\ kg^{-1}$, about 180 cm of soil is needed to adsorb 100% of the downward-moving NH_4^+ per year, com-
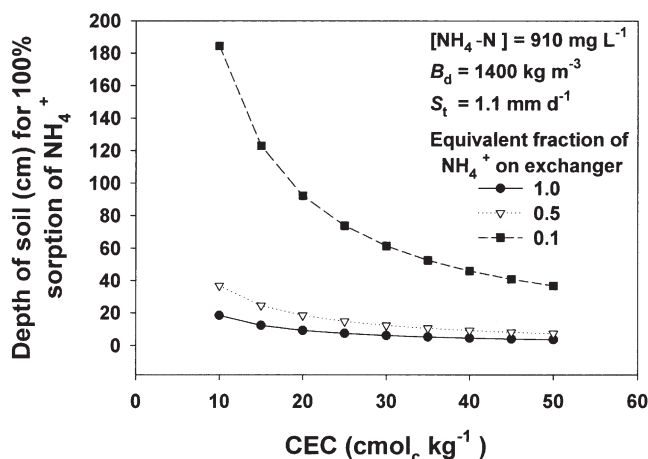
Fig. 1. Simulation of the depth of soil (Z_{eq}; Eq. [1]) needed to adsorb 100% of the NH_4^+ moving into the underlying soil of a swine-waste lagoon under various soil conditions after 1 yr. B_d, bulk density of the soil; S_t, whole-lagoon seepage rate; CEC, cation exchange capacity.

pared with 40 cm of soil if the EFA is 0.5. Also, a 75-cm reduction in Z_{eq} is achieved when the EFA of a 20 $cmol_c$ kg^{-3} soil is increased from 0.1 to 0.5. The model and Fig. 1 clearly show that increasing the EFA, CEC, or both can greatly reduce the amount of soil needed to adsorb downward-moving NH_4^+. Therefore, when evaluating soils for use as liners, choosing soils or soil amendments that improve protection of ground water quality by way of soil chemical properties should be considered. Thus, the objectives of this research were to (i) develop the methodology to evaluate two soils on their ability to selectively adsorb NH_4^+ by using binary (Ca^{2+}–K^+, Ca^{2+}–NH_4^+, and K^+–NH_4^+) and ternary exchange (Ca^{2+}–K^+–NH_4^+) reactions; (ii) evaluate these soils with amendments of bentonite or zeolite; and (iii) use the ternary model and information from actual swine- and cattle-waste lagoons to predict the depth of soil needed to adsorb 100% of the downward-moving NH_4^+.

MATERIALS AND METHODS

Laboratory

Binary exchange relationships (Ca^{2+}–K^+, Ca^{2+}–NH_4^+, and K^+–NH_4^+) were determined on two noncalcareous soils, hereafter referred to as exchangers, from the Great Plains region. Both soils were previously approved for use as compacted soil liners for animal-waste lagoon construction. Soil 1 (S1) was supplied by Kansas Livestock Association Environmental Services (Salina, KS), and was collected in Reno County, Kansas. Soil 2 (S2) was supplied by Agricultural Engineering Associates (Uniontown, KS), and was collected in Brown County, Nebraska. Neither soil had been exposed to waste materials before laboratory experiments. The same binary exchange studies were also performed on soil–amendment mixtures, also referred to as exchangers. The two amendments were a Na-bentonite (Envirogel 200; Wyo-Ben, Billings, MT) and clinoptilolite zeolite (BR-40; ZEO, McKinney, TX). The bentonite used for this study was in powder form where 98% of the product was less than 0.18 mm and the zeolite used for this study had a diameter of less than 0.425 mm. The CEC values of the bentonite and zeolite materials were determined

from Ca^{2+}–K^+ exchange following the methods used to determine binary exchange reactions below and were 40 and 67 $cmol_c kg^{-1}$, respectively. The determined CEC values for these bentonite and zeolite materials may differ from reported CEC values of other Na-bentonites and clinoptilolite zeolites based on the choice of indicator and replacement cations and also the length of time used for cation extraction (Kithome et al., 1998; Sposito et al., 1983). Individual amendments were mixed with each soil at a concentration of 60 g kg^{-1}, in accordance with bentonite mixture ratios used for sealing pond liners (USDA, 2002). Bentonite can be added during liner construction to decrease hydraulic conductivity and zeolite was selected because of its high values of CEC and its preference for NH_4^+ over Ca^{2+} and Na^+ (Howery and Thomas, 1965; Ming and Mumpton, 1989; Vucinic and Tomanec, 1997).

The <2.0-mm fractions of S1 and S2 were analyzed for sand, silt, and clay following the pipet method outlined in Gee and Bauder (1986). The soils were pretreated in an 80°C water bath with 30% H_2O_2 and 1 M NaOAc to remove organic matter and carbonates before the determination of the clay concentration. The difference between 1000 g kg^{-1} and the sum of the sand (>53 μm) and silt (2–53 μm) concentrations was determined to be the concentration of clay (<2 μm). Concentrations of sand, silt, and clay in the Soil 1 + bentonite (S1B), Soil 1 + zeolite (S1Z), Soil 2 + bentonite (S2B), and Soil 2 + zeolite (S2Z) soils were determined by using a modified hydrometer method of Gee and Bauder (1986). The clay fraction was determined by taking a hydrometer reading at a time determined by Stokes' law (about 8 h) after mixing. After the clay fraction was determined, the sand fraction was separated with a 53-μm sieve, and the mass of sand was determined by gravimetric methods after drying at 105°C for 24 h. Silt was determined to be the difference between 1000 g kg^{-1} and the sum of the clay and sand fractions.

Mineralogies of the clay fraction of S1 and S2 were determined by using X-ray diffraction (XRD) techniques outlined in Ransom et al. (1988). The clay fractions from both S1 and S2 were composed of mica–smectite–kaolinite assemblages. Specific surface areas of the Mg-saturated clay fractions of S1 and S2 were determined according to a modified ethylene glycol monoethyl ether (EGME) method outlined in Carter et al. (1986) in which clays remained Mg-saturated instead of being Ca-saturated. Total C was determined by combustion (CN2000; LECO, St. Joseph, MI). Saturated hydraulic conductivities were determined once for each soil and soil plus amendment following ASTM Designation D 5084-90 (American Society for Testing and Materials, 1991).

Binary-exchange reactions were conducted on Ca- or K-saturated exchangers. One gram of the <1.0-mm size fraction of each exchanger was equilibrated with 4 L of a solution containing varying equivalences of Ca^{2+} and K^+, Ca^{2+} and NH_4^+, and K^+ and NH_4^+ (Tables 1 and 2) using a flow-through approach. Solutions were prepared using gravimetric methods from 2 M stock solutions of chloride salts and deionized water while maintaining a constant ionic strength of 0.05 mol L^{-1}. The flow-through system consisted of a 47-mm Teflon filter apparatus equipped with a 45-μm filter, peristaltic pump, and Mariotte bottle. For S1 and S2, eleven solutions were used for each binary-exchange reaction. Based on the information provided from the S1 and S2 reactions, S1B, S1Z, S2B, and S2Z were only equilibrated with five solutions. All equilibrations with exchangers were repeated twice and were conducted at 25°C. A 50-mL aliquot of each solution was removed before exposure with the exchanger and was saved for analysis. After equilibrations were achieved, each sample was washed with 100 mL of 95% ethanol. Cations were extracted from a 0.5-g subsample of each exchanger for 30 min using 10 mL of 0.5 M

Table 1. Binary-exchange (Ca–K, Ca–NH$_4$, and K–NH$_4$) solution and exchanger compositions for Soil 1 (S1†) and Soil 2 (S2‡).

Ca–K				Ca–NH$_4$				K–NH$_4$			
Solution concentration		Exchanger composition		Solution concentration		Exchanger composition		Solution concentration		Exchanger composition	
Ca	K	Ca	K	Ca	NH$_4$	Ca	NH$_4$	K	NH$_4$	K	NH$_4$
—— mol L^{-1} ——		—— mol kg^{-1} ——		—— mol L^{-1} ——		—— mol kg^{-1} ——		—— mol L^{-1} ——		—— mol kg^{-1} ——	
				S1							
0.018	0.000	0.102	0.000	0.018	0.000	0.098	0.000	0.000	0.049	0.000	0.173
0.016	0.005	0.085	0.022	0.016	0.005	0.088	0.017	0.005	0.046	0.026	0.148
0.014	0.011	0.079	0.034	0.014	0.010	0.080	0.029	0.010	0.040	0.045	0.130
0.012	0.016	0.071	0.046	0.013	0.015	0.072	0.047	0.015	0.034	0.061	0.109
0.011	0.022	0.063	0.056	0.011	0.020	0.067	0.052	0.019	0.030	0.081	0.088
0.009	0.025	0.057	0.064	0.009	0.025	0.062	0.065	0.023	0.025	0.097	0.068
0.007	0.032	0.052	0.076	0.007	0.030	0.053	0.084	0.030	0.020	0.114	0.049
0.005	0.038	0.048	0.089	0.005	0.035	0.045	0.097	0.034	0.015	0.123	0.040
0.004	0.043	0.037	0.099	0.004	0.042	0.035	0.112	0.038	0.010	0.146	0.022
0.002	0.047	0.027	0.122	0.002	0.046	0.024	0.133	0.042	0.005	0.152	0.012
0.000	0.053	0.000	0.167	0.000	0.051	0.000	0.182	0.046	0.000	0.168	0.000
				S2							
0.019	0.000	0.090	0.000	0.018	0.000	0.084	0.000	0.000	0.050	0.000	0.149
0.016	0.005	0.071	0.017	0.017	0.005	0.074	0.013	0.005	0.047	0.020	0.123
0.015	0.011	0.062	0.028	0.015	0.011	0.068	0.024	0.010	0.041	0.034	0.110
0.013	0.016	0.059	0.039	0.013	0.016	0.062	0.033	0.015	0.035	0.049	0.093
0.011	0.021	0.053	0.052	0.011	0.021	0.057	0.043	0.019	0.031	0.064	0.079
0.009	0.026	0.049	0.060	0.009	0.026	0.051	0.054	0.032	0.026	0.074	0.062
0.007	0.031	0.043	0.072	0.007	0.031	0.045	0.066	0.037	0.021	0.098	0.041
0.005	0.036	0.035	0.079	0.005	0.036	0.037	0.077	0.043	0.016	0.106	0.033
0.004	0.038	0.030	0.094	0.004	0.043	0.029	0.095	0.046	0.011	0.125	0.017
0.002	0.047	0.021	0.111	0.002	0.047	0.018	0.111	0.053	0.005	0.132	0.010
0.000	0.051	0.000	0.149	0.000	0.052	0.000	0.145	0.057	0.000	0.135	0.000

† Supplied by Kansas Livestock Association Environmental Services from Reno County, Kansas.
‡ Supplied by Agricultural Engineering Associates from Brown County, Nebraska.

Na-acetate. Calcium and K$^+$ concentrations in the solutions and the 0.5 M Na-acetate extract were determined with inductively coupled plasma–atomic emission spectroscopy (Accuris 141; Fisons Instruments, Beverly, MA). Ammonium N concentrations from solutions and exchanger extracts were determined by the salicylate–hypochlorite method (Crooke and Simpson, 1971) and were analyzed with an autoanalyzer (Alpkem, Clackamas, OR). The CEC value of each exchanger

Table 2. Binary-exchange (Ca–K, Ca–NH$_4$, and K–NH$_4$) solution and exchanger compositions for Soil 1 + bentonite (S1B†), Soil 1 + zeolite (S1Z‡), Soil 2 + bentonite (S2B§), and Soil 2 + zeolite (S2Z¶).
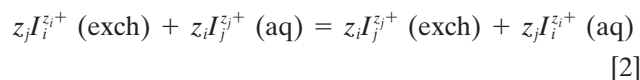
Ca–K				Ca–NH$_4$				K–NH$_4$			
Solution concentration		Exchanger composition		Solution concentration		Exchanger composition		Solution concentration		Exchanger composition	
Ca	K	Ca	K	Ca	NH$_4$	Ca	NH$_4$	K	NH$_4$	K	NH$_4$
—— mol L^{-1} ——		—— mol kg^{-1} ——		—— mol L^{-1} ——		—— mol kg^{-1} ——		—— mol L^{-1} ——		—— mol kg^{-1} ——	
				S1B							
0.018	0.006	0.089	0.025	0.016	0.005	0.096	0.017	0.005	0.046	0.035	0.164
0.013	0.018	0.070	0.060	0.012	0.015	0.087	0.039	0.017	0.036	0.073	0.116
0.009	0.029	0.061	0.073	0.009	0.026	0.066	0.067	0.028	0.025	0.100	0.077
0.005	0.040	0.042	0.107	0.005	0.036	0.052	0.100	0.036	0.016	0.135	0.040
0.002	0.051	0.024	0.138	0.002	0.047	0.028	0.141	0.047	0.005	0.167	0.009
				S1Z							
0.017	0.006	0.081	0.059	0.015	0.006	0.091	0.044	0.006	0.042	0.038	0.179
0.013	0.018	0.065	0.092	0.012	0.016	0.073	0.086	0.017	0.035	0.093	0.127
0.009	0.029	0.047	0.120	0.009	0.026	0.063	0.114	0.027	0.027	0.134	0.079
0.005	0.041	0.037	0.139	0.005	0.037	0.042	0.142	0.040	0.019	0.167	0.042
0.002	0.052	0.023	0.168	0.002	0.047	0.024	0.173	0.049	0.006	0.188	0.011
				S2B							
0.016	0.006	0.077	0.015	0.018	0.005	0.083	0.015	0.006	0.046	0.021	0.133
0.013	0.018	0.062	0.041	0.014	0.017	0.062	0.033	0.016	0.036	0.056	0.106
0.010	0.031	0.044	0.052	0.010	0.030	0.052	0.053	0.026	0.025	0.086	0.071
0.007	0.042	0.036	0.079	0.006	0.036	0.042	0.091	0.037	0.015	0.104	0.033
0.002	0.054	0.021	0.119	0.002	0.045	0.017	0.112	0.048	0.005	0.134	0.009
				S2Z							
0.018	0.007	0.065	0.048	0.018	0.006	0.068	0.041	0.006	0.046	0.028	0.172
0.014	0.019	0.050	0.078	0.014	0.018	0.059	0.079	0.016	0.036	0.071	0.119
0.010	0.030	0.039	0.109	0.010	0.030	0.047	0.102	0.027	0.026	0.104	0.075
0.006	0.043	0.024	0.123	0.006	0.036	0.036	0.130	0.038	0.016	0.127	0.037
0.002	0.053	0.014	0.151	0.002	0.045	0.018	0.162	0.048	0.005	0.152	0.010

† Supplied by Kansas Livestock Association Environmental Services from Reno County, Kansas, and amended with 60 g bentonite kg^{-1} soil.
‡ Supplied by Kansas Livestock Association Environmental Services from Reno County, Kansas, and amended with 60 g zeolite kg^{-1} soil.
§ Supplied by Agricultural Engineering Associates from Brown County, Nebraska, and amended with 60 g bentonite kg^{-1} soil.
¶ Supplied by Agricultural Engineering Associates from Brown County, Nebraska, and amended with 60 g zeolite kg^{-1} soil.

(cmol$_c$ kg^{-1}) after equilibration with a solution was determined to be the sum of the charges of the two cations from the binary reactions. Individual CEC values of all the binary reactions from respective exchangers were summed and divided by the total number of binary reactions to derive the average CEC for each exchanger.

THEORETICAL

Using the general binary exchange reaction, as outlined by Bond (1995) and Bond and Verburg (1997), of:

$$z_j I_i^{z_i+} \ (\text{exch}) + z_i I_j^{z_j+} \ (\text{aq}) = z_i I_j^{z_j+} \ (\text{exch}) + z_j I_i^{z_i+} \ (\text{aq}) \qquad [2]$$

where z_i is the valence of cation I_i and (exch) and (aq) are the exchanger and solution phases, respectively, the Vanselow selectivity coefficients (K_V) and equivalent fractions of cations on the exchanger (N_i) were computed for each binary exchange reaction as defined by Sparks (2003). Solution concentrations were used to calculate solution-phase ionic strengths and the Davies equation was used to calculate the single-ion activity coefficients used to estimate activities from concentrations (Sparks, 2003). Binary-exchange isotherms were constructed according to the approach outlined in Sparks (2003), in which the equivalent fraction on the exchanger phase was plotted as a function of the equivalent fraction in the solution phase. Each exchange isotherm is the average of the two replications. Nonpreference exchange isotherms for the divalent–univalent mixtures were calculated according to the approach outlined in Sposito (2000). Nonpreference isotherms for the univalent–univalent exchanges were 1:1 lines. Gibb's free energies (ΔG_{ex}) were calculated for each binary-exchange reaction from:

$$\ln K_{ex} = \int_0^1 K_v dN_i \qquad [3]$$

and:

$$\Delta G_{ex}^0 = -RT \ln K_{ex} \qquad [4]$$

where K_{ex} is the equilibrium exchange constant; R is equal to 8.314 J mol^{-1} K^{-1}; and T (K) is the reaction temperature (Sparks, 2003). Each reported Gibb's free-energy value is the average of two replications.

The Rothmund–Kornfeld approach outlined in Bond (1995) and Bond and Verburg (1997) was followed, and ternary exchange between Ca^{2+}–K$^+$–NH$_4^+$ was predicted from Gaines–Thomas binary-exchange reactions (Ca^{2+}–K$^+$, Ca^{2+}–NH$_4^+$, and K$^+$–NH$_4^+$). The Gaines–Thomas working form of the Rothmund–Kornfeld equation is:

$$k_{ij} = \frac{N_j^{z_i}}{N_i^{z_j}} \left[\frac{(\gamma_i C_i)^{z_j}}{(\gamma_j C_j)^{z_i}} \right]^{n_{ij}} \qquad [5]$$

where γ_i is the activity coefficient of cation I_i in the solution phase; C is the concentration of cation I_i in the solution phase in mol L^{-1}; and k_{ij} and n_{ij} are the Rothmund–Kornfeld empirical exchange constants. Using the linear model:

$$\log\left(\frac{N_j^{z_i}}{N_i^{z_j}}\right) = \log k_{ij} + n_{ij} \log\left[\frac{(\gamma_j C_j)^{z_i}}{(\gamma_i C_i)^{z_j}}\right] \qquad [6]$$

the Rothmund–Kornfeld empirical exchange constants were determined by fitting the binary data to a plot of:

$$\log\left(\frac{N_j^{z_i}}{N_i^{z_j}}\right) \text{ vs. } \log\left[\frac{(\gamma_j C_j)^{z_i}}{(\gamma_i C_i)^{z_j}}\right] \qquad [7]$$

where $\log k_{ij}$ and n_{ij} are the intercept and slope, respectively. The empirical exchange constants are then used to solve for the predicted ratios of cations on the exchanger phase N_K/N_{NH_4}, N_{Ca}/N_K^2, and $N_{Ca}/N_{NH_4}^2$ by:

$$\frac{(N_K)}{(N_{NH_4})} = k_{K-NH_4} \left[\frac{(A_K)}{(A_{NH_4})}\right]^{n_{K-NH_4}} \qquad [8a]$$

$$\frac{(N_{Ca})}{(N_K)^2} = k_{Ca-K} \left[\frac{(A_{Ca})}{(A_K)^2}\right]^{n_{Ca-K}} \qquad [8b]$$

$$\frac{(N_{Ca})}{(N_{NH_4})^2} = k_{Ca-NH_4} \left[\frac{(A_{Ca})}{(A_{NH_4})^2}\right]^{n_{Ca-NH_4}} \qquad [8c]$$

where A is the solution phase activity ($\gamma_i C_i$) in a ternary solution. Predicted equivalent fractions of each cation on the exchanger phase are then determined by describing the mass balance of the exchanger phase as:

$$N_K + N_{NH_4} + N_{Ca} = 1 \qquad [9]$$

and solving the following quadratic equations:

$$N_K^2 + N_K\left(\frac{\alpha + 1}{\alpha\beta}\right) - \frac{1}{\beta} = 0 \qquad [10a]$$

$$N_{NH_4}^2 + N_{NH_4}\left(\frac{\alpha + 1}{\eta}\right) - \frac{1}{\eta} = 0 \qquad [10b]$$

$$N_{Ca} + N_{Ca}^{0.5}\lfloor(\beta)^{-0.5} + (\eta)^{-0.5}\rfloor - 1 = 0 \qquad [10c]$$

where $\alpha = N_K/N_{NH_4}$, $\beta = N_{Ca}/N_K^2$, and $\eta = N_{Ca}/N_{NH_4}^2$. Through the use of Eq. [9] and [10], there are $n + 1$ equations for n unknowns, which makes it possible to calculate the three equivalent fractions of cations on the exchanger using only Eq. [9] and two of Eq. [10] (Bond and Verburg, 1997). Validity of the model was evaluated by equilibrating the exchanger phases with a ternary solution containing equal equivalences of Ca^{2+}, K$^+$, and NH$_4^+$. Also, each exchanger was equilibrated with solutions containing high equivalences (0.69) of each cation, Ca^{2+}, K$^+$, or NH$_4^+$, while keeping equivalent fractions of the remaining cations constant. All ternary solutions were prepared with a target ionic strength of 0.05 mol L^{-1} and repeated twice. In addition, each exchanger was equilibrated with the previously described four solutions containing a background Na$^+$ concentration of 0.013 mol L^{-1}. Additions of Na$^+$ to binary-exchange reactions have been shown to not influence the exchangers' cationic preference (Sposito et al., 1983). This concentration of Na$^+$ is similar to what one may expect in swine and cattle waste lagoons in Kansas (Ham, 2002). All equilibrium reactions were conducted twice, and the reaction temperature was held constant at 25°C. Finally, lagoon-liquor data from existing swine and cattle waste lagoons in Kansas were used to predict the equivalent fractions of Ca^{2+}, K$^+$, and NH$_4^+$ on the exchanger phase. These results were used in conjunction with Eq. [1] to predict the depth of soil needed (cm) to adsorb 100% of the downward-moving NH$_4^+$ after 20 yr of operation.

RESULTS AND DISCUSSION

Characterization of Exchangers

The clay contents of S1 and S2 were 354 and 239 g kg^{-1}, respectively (Table 3). The addition of bentonite increased the concentration of clay in the S1 and S2 soils whereas the addition of zeolite decreased the concentration of clay. Addition of the amendments slightly decreased the total C in the S1, S1B, and S1Z ex-

Table 3. Select chemical and physical parameters of two Great Plains soils (S1 and S2) alone, and with additions of bentonite (B; addition of 60 g bentonite kg^{-1}) or zeolite (Z; addition of 60 g zeolite kg^{-1}).

Exchanger	Sand	Silt	Clay	Total C	CEC†	Saturated hydraulic conductivity	Specific surface area of the clay
	g kg^{-1}				cmol$_c$ kg^{-1}	cm s^{-1}	m^2 g^{-1}
S1	139	506	354	7.8	17.9	2.93×10^{-8}	334
S1B	148	148	368	7.2	19.4	4.47×10^{-8}	
S1Z	207	207	352	7.0	21.9	3.54×10^{-8}	
S2	386	375	239	4.0	15.1	1.72×10^{-8}	361
S2B	389	389	247	4.1	15.6	1.43×10^{-8}	
S2Z	464	464	221	4.0	18.3	2.07×10^{-7}	

† Cation exchange capacity.

changers, from 7.8 g kg^{-1} to 7.2 and 7.0 g kg^{-1}, respectively (Table 3). The total C remained fairly constant at about 4.0 g kg^{-1} in the S2, S2B, and S2Z exchangers.

The addition of the bentonite and zeolite amendments increased the CEC value of S1 from 17.9 cmol$_c$ kg^{-1} to 19.4 and 21.9 cmol$_c$ kg^{-1}, respectively (Table 3). Although the addition of bentonite only increased the average CEC of S2 by 0.5 cmol$_c$ kg^{-1}, the addition of zeolite increased the CEC by 3.2 cmol$_c$ kg^{-1} (Table 3). The saturated hydraulic conductivities of S1 and S2 were influenced by the addition of the amendments. The saturated hydraulic conductivity of S1 was 2.93×10^{-8} cm s^{-1} (Table 3). The addition of bentonite and zeolite to S1 slightly increased and decreased the saturated hydraulic conductivities, respectively. As would be expected with the addition of bentonite to soil, the saturated hydraulic conductivity of S2B was 0.29×10^{-8} cm s^{-1} lower than that of S2 (Table 3). Addition of the more granular zeolite material to S2 increased the saturated hydraulic conductivity by about 12 times, initially making S2Z undesirable for liner construction because it exceeded the critical value of 1×10^{-7} cm s^{-1} (Table 3) (USDA, 1992). Although, Ham and DeSutter (1999) determined that laboratory-derived saturated hydraulic conductivities might be as much as five times greater than those calculated from whole-lagoon seepage test results. The specific surface areas of the clay fractions of S1 and S2 were 334 and 361 m^2 g^{-1}, respectively (Table 3).

Binary Exchange

The repeatability of the cation concentrations on the exchangers was generally less than a 10% relative percent difference (RPD) from the means indicating that the flow-through method worked very well for equilibrating an exchanger phase with a solution phase. Thus, the average of the two replications was reported (Tables 1 and 2). For S1 and S2, complete exchange of the initial saturating cation was observed for all reactions when the saturating cation was not present in the equilibrating solutions (Table 1). Because of this behavior, equivalent fractions of 1.0 and 0.0 were added to the S1B, S1Z, S2B, and S2Z datasets to allow the ΔG_{ex}^0 to be calculated for all six exchangers to be comparable. The RPD from the means of the ΔG values, reported in Fig. 2 through 4, indicate that the smallest RPD was from Ca^{2+}–K$^+$ exchange reaction on the S2B exchanger (0.3%) and the largest RPD was from the K$^+$–NH$_4^+$ exchange reaction on the S1B exchanger (44.7%). In general, most RPDs for the ΔG_{ex}^0 values were less than 10%.

Binary-exchange isotherms for S1, S1B, and S1Z were all below the nonpreference isotherms, indicating exchanger preference for K$^+$ over Ca^{2+} for the Ca^{2+}–K$^+$ exchange reaction (Fig. 2a). Gibb's free-energy calculations supported this conclusion where ΔG_{ex}^0 values for S1, S1B, and S1Z exchangers were −4.66, −5.36, and −8.17 kJ mol^{-1}, respectively. The exchange isotherm and the ΔG_{ex}^0 value for the S1Z exchanger were lower and about 1.5 times more negative, respectively, than the exchange isotherms and ΔG_{ex}^0 values for the S1 and S1B exchangers, indicating a stronger preference for K$^+$ over Ca^{2+} when zeolite was present. Exchange isotherms and ΔG_{ex}^0 values also indicate that K$^+$ is preferred over Ca^{2+} on the S2, S2B, and S2Z exchangers (Fig. 2b). Again, S2Z had the greatest preference for K$^+$ over Ca^{2+} compared with the S2 and S2B exchangers as observed by the exchange isotherm and a ΔG_{ex}^0 value of −8.99 kJ mol^{-1}.

Isotherms and ΔG_{ex}^0 values both indicate a preference for NH$_4^+$ over Ca^{2+} for the S1, S1B, and S1Z exchangers (Fig. 3a). The addition of zeolite to the S1 exchanger increased NH$_4^+$ preference over both the S1 and S1B exchangers (Fig. 3a). Exchanger S2Z had the greatest preference for NH$_4^+$ over Ca^{2+}, as indicated by the exchange isotherm and a ΔG_{ex}^0 value of −8.50 kJ mol^{-1} (Fig. 3b). The addition of bentonite to both the S1 and S2 exchangers had little affect on the preference of S1B and S2B exchangers for NH$_4^+$ over Ca^{2+} (Fig. 3a and 3b).

Exchange isotherms and ΔG_{ex}^0 values indicated a slightly greater preference for K$^+$ over NH$_4^+$ for all six exchangers (Fig. 4). Addition of bentonite and zeolite to S1 numerically increased the ΔG_{ex}^0 values for K$^+$ over NH$_4^+$, but statistical differences were not determined (Fig. 4a). Gibb's free energy values for the S2, S2B, and S2Z exchangers were very similar (Fig. 4b).

Ternary Exchange

Binary-exchange data were used to calculate the intercept and slope, log k_{ij} and n_{ij}, respectively, of the plot of Eq. [7] (Table 4). The r^2 values of these plots indicate a good fit of the log-transformed data. Values of r^2 ranged from 0.985 to 0.999 from all the plots. Thus, the determined values of k_{ij} and n_{ij} can be considered good estimates of the empirical exchange constants. Through the use of Eq. [8], [9], and [10], k_{ij} and n_{ij} were used to estimate N_i for each cation in a ternary system. These predicted N_i values were compared with the measured N_i for each cation in the ternary system. The relationship between the predicted and measured N_i on the S1 ex-
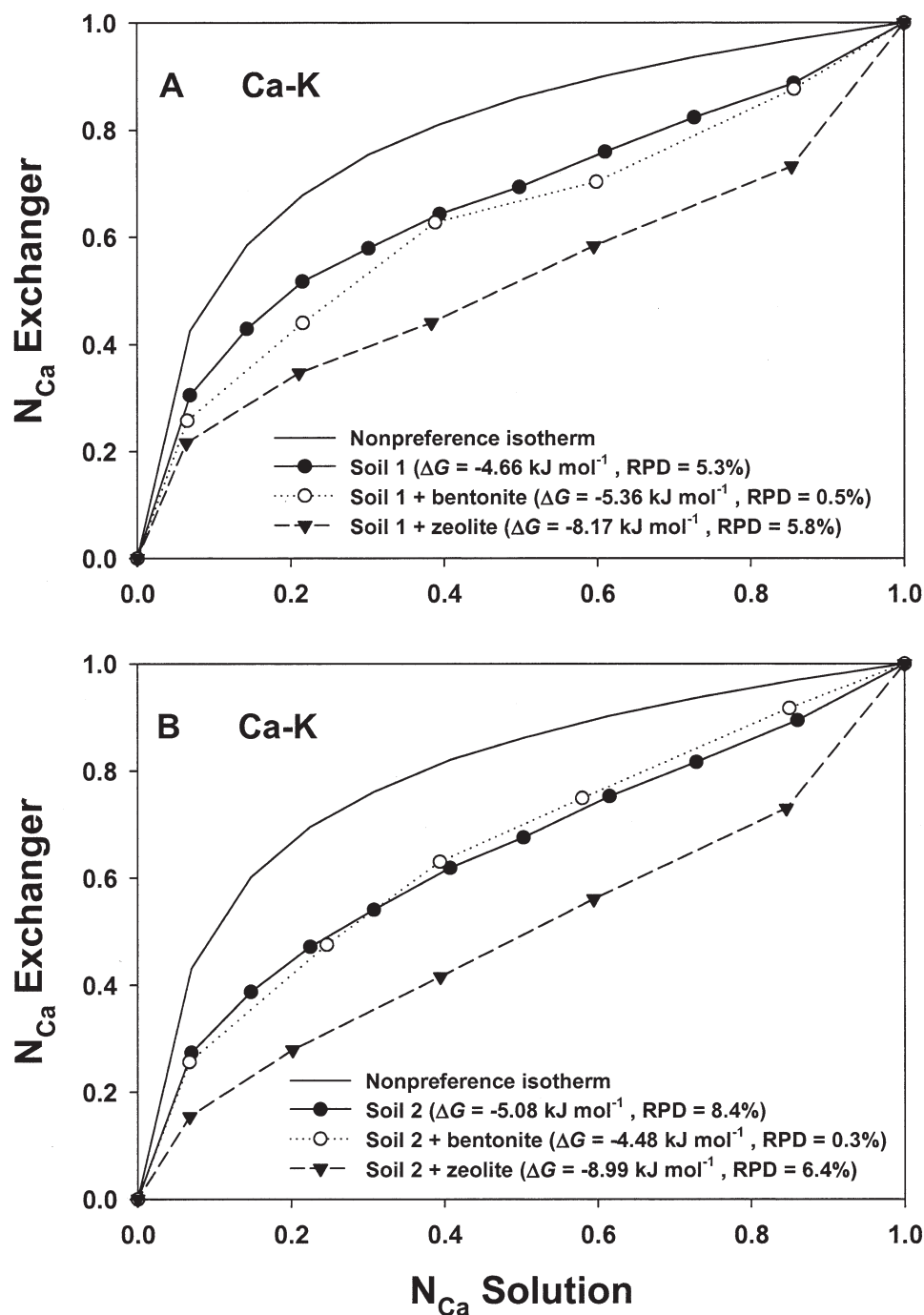
Fig. 2. Calcium–K⁺ exchange isotherms and values for the Gibb's free energy of exchange (ΔG) for two Great Plains soils: S1 (a) and S2 (b) alone, and with the addition of bentonite and zeolite at a concentration of 60 g kg⁻¹. The relative percent difference (RPD) from the mean of the ΔG values is presented.

changer was very good, with an r^2 of 0.966 and a root-mean square (RMS) of 0.038 (Fig. 5a). The addition of bentonite did not hinder the predictability of N_i, but addition of zeolite decreased the r^2 value to 0.881 and increased the RMS to 0.055. Adding a Na⁺ background to the equilibrium solutions did not decrease the model's ability to predict N_i in a ternary system (Fig. 5b). Both the r^2 and RMS values of S1 and S1B slightly improved when Na was present in solution, although the r^2 and RMS values from the S1Z exchanger slightly deterio-

rated with the presence of Na⁺ in the solution. No significant differences were observed between the exchangers with, and without, Na⁺ present in the solution phase (data not shown).

The Rothmund–Kornfeld approach also worked very well for predicting N_i on the S2, S2B, and S2Z exchangers, compared with the measured results. Values of r^2 were 0.975 and 0.972 for the S2 and S2B exchangers, respectively, with RMS values less than 0.04 (Fig. 6a). Although the addition of zeolite decreased the r^2 value
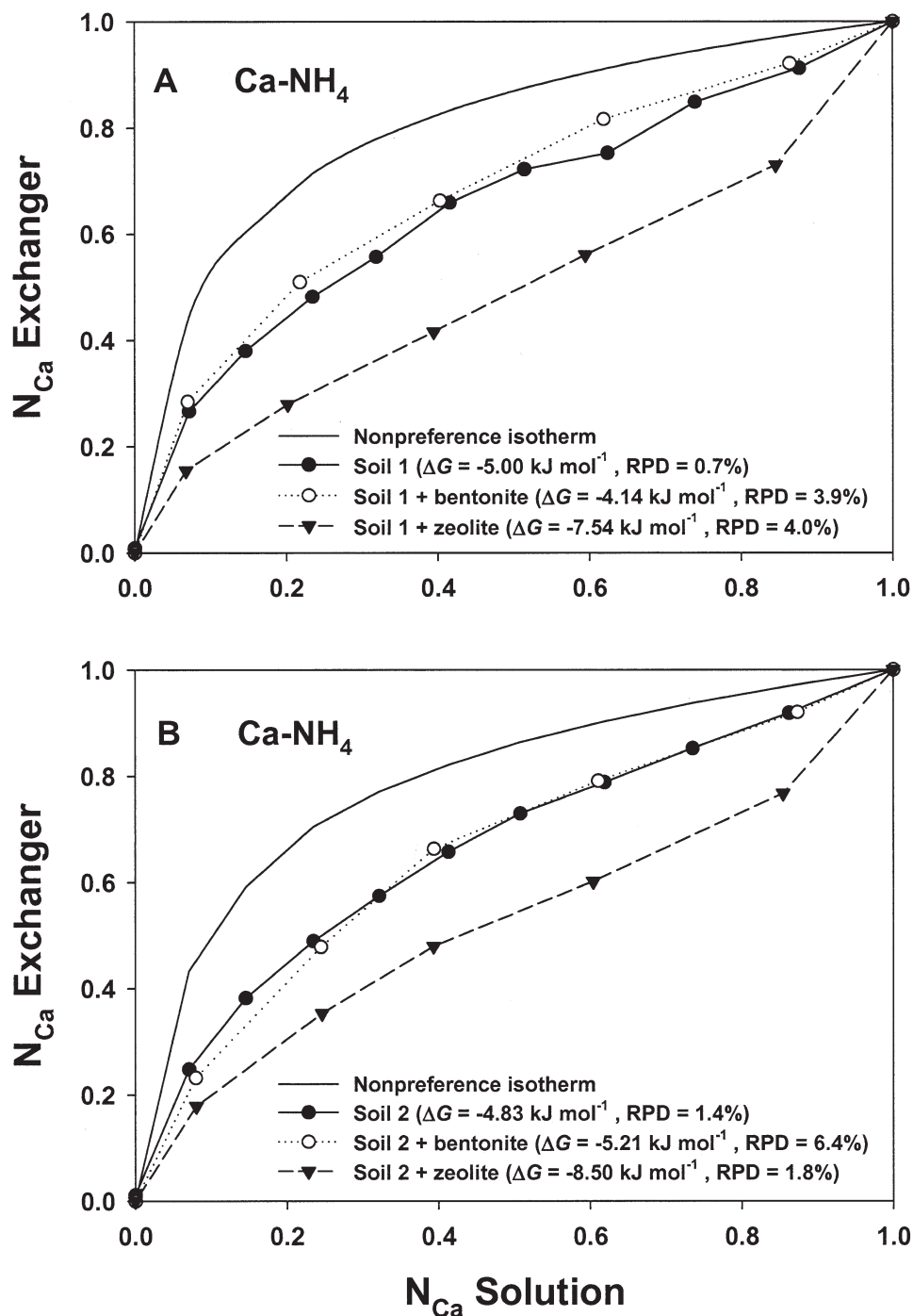
Fig. 3. Calcium–NH_4^+ exchange isotherms and values for the Gibb's free energy of exchange (ΔG) for two Great Plains soils: S1 (a) and S2 (b) alone, and with the addition of bentonite and zeolite at a concentration of 60 g kg^{-1}. The relative percent difference (RPD) from the mean of the ΔG values is presented.

to 0.859, the Rothmund–Kornfeld method still provided a good estimate of N_i on the S2Z exchanger. The addition of 0.013 mol Na L^{-1} to the solution phase slightly decreased the r^2 value and increased the RMS value for the S2B exchanger (Fig. 6b). Although the S2 exchanger was relatively unchanged by addition of Na$^+$, the r^2 value slightly increased with the S2Z exchanger, to 0.918. Again, no significant differences were observed between the exchangers with, and without, Na$^+$ present in the solution phase (data not shown).

Application of the Rothmund–Kornfeld Approach

The binary and ternary assessments of the six exchangers, in conjunction with Eq. [1], were applied to make predictions of the equivalent depth of soil needed to retain 100% of the NH_4^+ seeping from four animal waste lagoons in Kansas. This approach assumes piston displacement of the existing soil water with the incoming fluid where molecular diffusion and hydrodynamic dispersion are not considered. Swine 1 and Swine 2 were
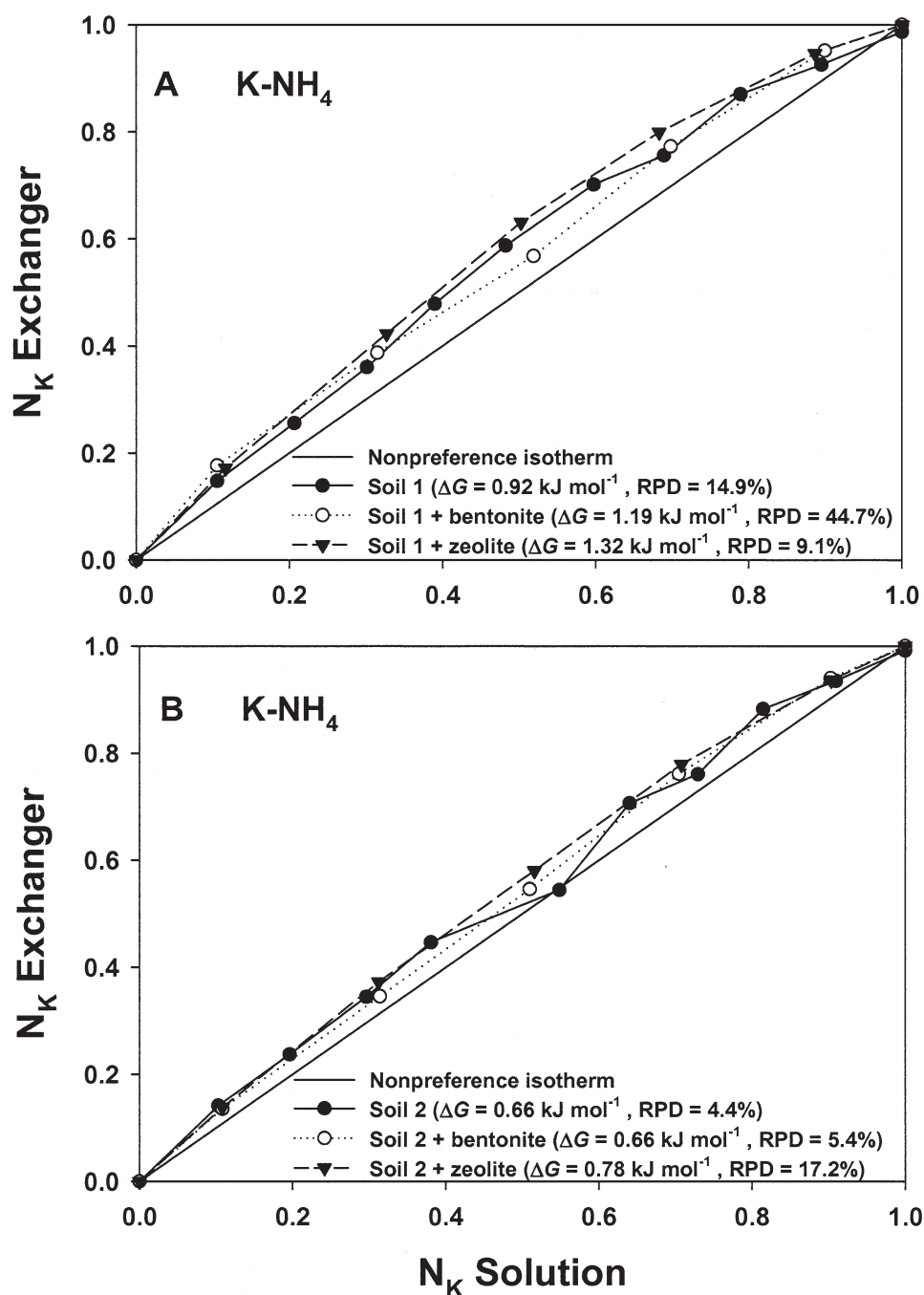
Fig. 4. Potassium–NH_4^+ exchange isotherms and values for the Gibb's free energy of exchange (ΔG) for two Great Plains soils: S1 (a) and S2 (b) alone, and with the addition of bentonite and zeolite at a concentration of 60 g kg^{-1}. The relative percent difference (RPD) from the mean of the ΔG values is presented.

finishing and nursery operations, respectively, located in southwestern Kansas. Cattle 1 and Cattle 2 were runoff lagoons located in central and southwestern Kansas, respectively. The concentration of NH_4^+ in the swine lagoons was as much as six times greater than in the cattle lagoons, whereas Ca^{2+} concentrations were greater in the cattle lagoons (Table 5). Potassium concentrations were more consistent in the cattle lagoons than in the swine lagoons.

The information provided in Table 5 was inserted into the Rothmund–Kornfeld model for each soil and soil-

plus-amendment combination to predict the equivalent fraction of NH_4^+ on the exchangers (N_{NH_4}). The predicted N_{NH_4} value for each exchanger was inserted into Eq. [1], along with the concentration of NH_4^+ in the waste, to estimate the equivalent depth of soil needed to retain 100% of the NH_4^+ that would be predicted to seep from each lagoon over 20 yr. The bulk density of the soil was assumed to be 1300 kg m^{-3}. Estimated exchanger N_{NH_4} values from the Swine 1 lagoon were very similar, with values ranging from 0.51 to 0.60 (Table 6). From these exchangers, S1Z and S2Z had the highest N_{NH_4} values,

Table 4. Rothmund–Kornfeld fitted parameters for the Gaines–Thomas convention for two Great Plains soils (S1 and S2) alone, and with additions of bentonite (B; addition of 60 g bentonite kg^{-1}) or zeolite (Z; addition of 60 g zeolite kg^{-1}).

| Binary exchange	k_{gt}	n_{gt}	r^2
	S1		
Ca–K	149.50	0.71	0.998
Ca–NH$_4$	214.26	0.81	0.993
K–NH$_4$	1.46	1.04	0.991
	S1B		
Ca–K	122.49	0.72	0.992
Ca–NH$_4$	320.89	0.84	0.997
K–NH$_4$	1.62	1.05	0.985
	S1Z		
Ca–K	19.01	0.52	0.990
Ca–NH$_4$	39.77	0.62	0.996
K–NH$_4$	1.81	1.06	0.989
	S2		
Ca–K	167.00	0.78	0.999
Ca–NH$_4$	336.18	0.88	0.999
K–NH$_4$	1.32	1.03	0.985
	S2B		
Ca–K	251.20	0.82	0.995
Ca–NH$_4$	350.74	0.90	0.987
K–NH$_4$	1.36	1.07	0.996
	S2Z		
Ca–K	23.65	0.60	0.986
Ca–NH$_4$	33.70	0.64	0.989
K–NH$_4$	1.44	1.05	0.994

Fig. 5. (a) Equivalent fraction of cations on the Soil 1 (S1), Soil 1 + bentonite (S1B), and Soil 1 + zeolite (S1Z) exchanger phases predicted from the Rothmund–Kornfeld equation and Gaines–Thomas convention vs. laboratory-measured equivalent fractions on the S1, S1B, and S1Z exchangers. (b) Also with Na added to the ternary solutions at 0.013 mol L^{-1}. Root-mean square (RMS) = $[(\Sigma \text{ predicted N} - \text{measured N})^2/n]^{0.5}$.

with 0.55 and 0.60, respectively. The range of exchanger N_{NH_4} values from Swine 2, which had 2.57 and 2.86 cmol$_c$ L^{-1} more NH$_4^+$ and K$^+$, respectively, in the liquor than did Swine 1, were from 0.46 to 0.52. The addition of the amendments did not increase the N_{NH_4} values above those of the native soils with Swine 2.

The predicted N_{NH_4} values for the cattle lagoons were about half of the swine-lagoon values (Table 6) due to the much lower NH$_4^+$ concentrations in the cattle-lagoon liquor than in the swine lagoon liquor (Table 5). Also, in conjunction with the NH$_4^+$ concentrations, overall N_{NH_4} values from the Cattle 1 were less than values from Cattle 2. In Cattle 1 and Cattle 2, the addition of zeolite increased the N_{NH_4} values for S1 and S2 by up to 0.05 and 0.1, respectively. But the addition of bentonite to S1 and S2 decreased or did not change the N_{NH_4} values above values of the native soils. Overall, the addition of bentonite only increased N_{NH_4} values 50% of the time whereas addition of zeolite increased the N_{NH_4} values 75% of the time. However, the range of N_{NH_4} values for S1 and S2 with and without amendments is relatively small, and indicates that the amendments used here did not greatly increase the exchangers' selectivity for NH$_4^+$.

Although the benefit of adding bentonite and zeolite to soils with respect to the predicted N_{NH_4} values may be small, these slight increases (Table 6), coupled with increases in CEC (Table 3), will ultimately decrease the depth of soil needed to adsorb downward-moving NH$_4^+$. The value of Z_{eq} required after 20 yr for the six exchangers ranged between 223 and 318 cm for Swine 1 and between 425 and 545 cm for Swine 2 (Table 6). For both Swine 1 and Swine 2, the benefit of adding bentonite to the native soils was very subtle, but the addition of zeolite to S1 and S2 decreased Z by 55 and
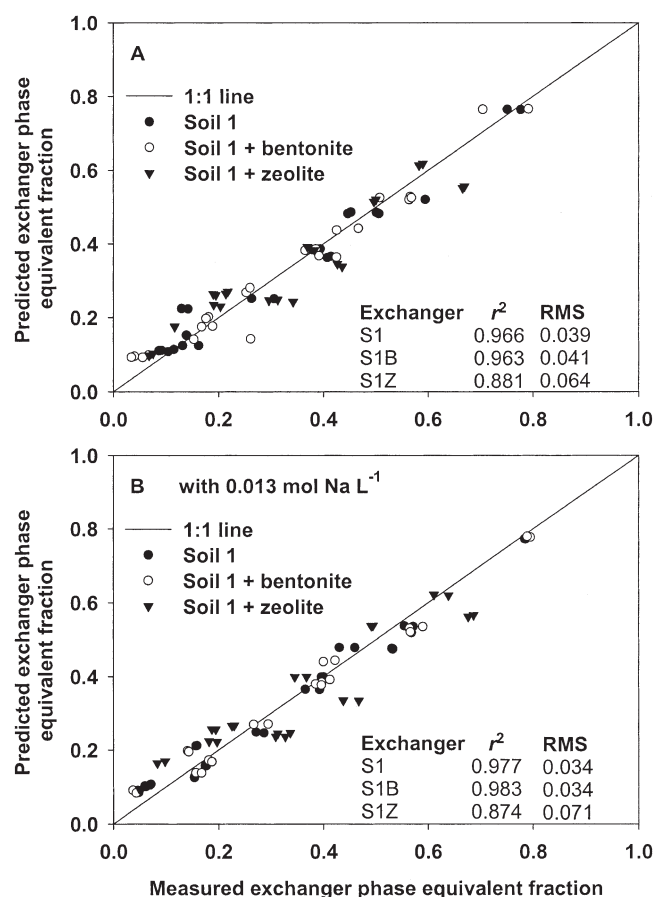
73 cm, respectively, in the Swine 1 lagoon. Although Z_{eq} was as much as two times greater in Swine 2 than in Swine 1, the trend of results was very similar. Bentonite additions to S1 and S2 did very little in decreasing Z_{eq} for Swine 2, but additions of zeolite reduced the required depth by up to 86 cm. Bentonite additions only decreased Z_{eq} in the S2B exchangers over the S2 in both cattle lagoons by 10 cm or less (Table 6). Conversely, the S1B exchangers for both cattle lagoons slightly increased the predicted amount of soil, compared with S1. Again, zeolite additions to S1 and S2 greatly decreased Z_{eq} for both lagoons by as much as 133 cm, compared with the Z_{eq} of the native soils.

Overall, additions of bentonite to the native soils were not very effective at reducing Z_{eq} in any of the lagoons. Considering all S1B and S2B combinations with lagoons, the average reduction in Z_{eq} was only about 6 cm, although additions of zeolite to both soils decreased the Z_{eq} from all lagoons by an average of about 78 cm when compared with that of the native soils. Thus, from a soil chemistry perspective, the benefits of adding bentonite to the soil to reduce Z_{eq} may not be as important as the beneficial decrease of a soil's saturated hydraulic
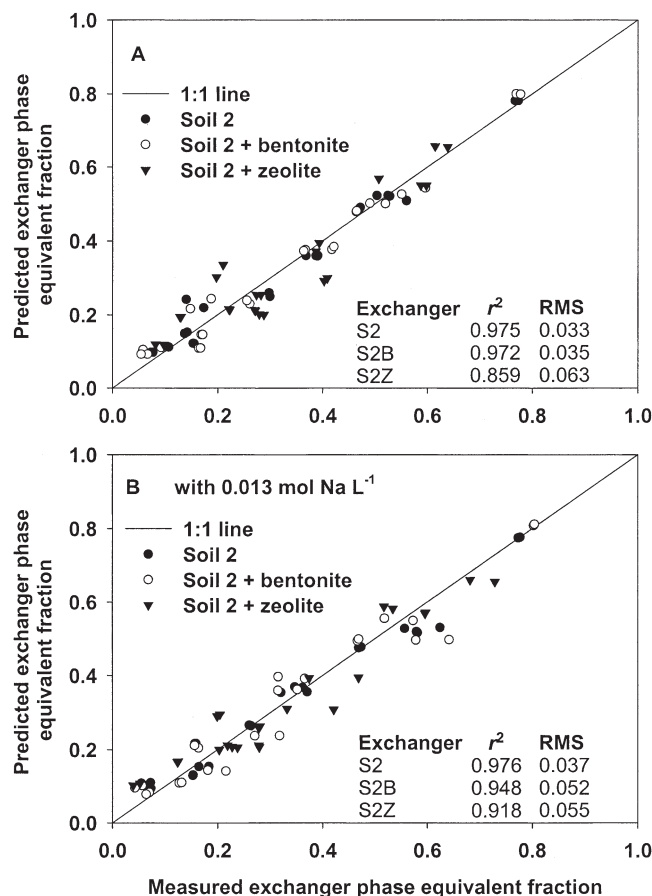
Fig. 6. (a) Equivalent fraction of cations on the Soil 2 (S2), Soil 2 + bentonite (S2B), and Soil 2 + zeolite (S2Z) exchanger phases predicted from the Rothmund–Kornfeld equation and Gaines–Thomas convention vs. laboratory-measured equivalent fractions on the S2, S2B, and S2Z exchangers. (b) Also with Na added to the ternary solutions at 0.013 mol L^{-1}. Root-mean square (RMS) = [(Σ predicted N − measured N)^2/n]$^{0.5}$.

conductivity (Table 3). Conversely, zeolite additions to native soil greatly decreased the required Z_{eq} under lagoons, which can mostly be attributed to increases in the CEC of the mixtures. Additions of zeolite, however, did tend to increase the saturated hydraulic conductivities of the soil and may not be appropriate for use with some soils.

CONCLUSIONS

The CEC of native soils may be increased through the use of amendments such as bentonite and zeolite. Additions of zeolite at a rate of 60 g kg^{-1} to two soils

Table 5. Cation concentrations in two swine and two cattle-feedlot runoff lagoons.

Lagoon	Ca	K	NH$_4$
		cmol$_c$ L^{-1}	
Swine 1	0.55	1.37	4.36
Swine 2	0.40	4.23	6.93
Cattle 1	0.75	1.76	1.21
Cattle 2	1.60	1.57	1.86

Table 6. Predicted equivalent fraction of NH$_4$ (N_{NH_4}) on an exchanger in a ternary system according to the Rothmund–Kornfeld approach, and the estimated depth of soil (Z_{eq}) needed after 20 yr to retain 100% of the NH$_4$–N seeping from four animal waste lagoons.

Exchanger†	N_{NH_4}	Z_{eq}‡
		cm
	Swine 1 lagoon	
S1	0.54	278
S1B	0.51	272
S1Z	0.55	223
S2	0.56	318
S2B	0.57	303
S2Z	0.60	245
	Swine 2 lagoon	
S1	0.50	478
S1B	0.47	469
S1Z	0.46	425
S2	0.52	616
S2B	0.52	528
S2Z	0.51	459
	Cattle 1 lagoon	
S1	0.21	200
S1B	0.19	203
S1Z	0.23	149
S2	0.20	248
S2B	0.20	240
S2Z	0.26	158
	Cattle 2 lagoon	
S1	0.25	256
S1B	0.22	269
S1Z	0.30	175
S2	0.24	317
S2B	0.24	307
S2Z	0.34	184

† Two Great Plains soils (S1 and S2) alone, and with additions of bentonite (B; addition of 60 g bentonite kg^{-1}) or zeolite (Z; addition of 60 g zeolite kg^{-1}).
‡ Estimated depth was determined by using a soil bulk density of 1300 kg m^{-3} and a seepage rate of 1.1 mm d^{-1}.

that were previously approved for use as compacted soil liners increased the CEC of the mixtures by as much as 4.0 cmol$_c$ kg^{-1}. Binary-exchange reactions between Ca^{2+}–K$^+$, Ca^{2+}–NH$_4^+$, and K$^+$–NH$_4^+$ that were conducted on these soils, and soils plus amendments, indicated that the univalent cations, K$^+$ and NH$_4^+$, were preferred over Ca^{2+} on the exchangers. Also, K$^+$ was preferred over NH$_4^+$ in all instances. Mixtures of soil plus zeolite consistently had the greatest preference for K$^+$ or NH$_4^+$ over Ca^{2+} and for K$^+$ over NH$_4^+$, compared with preferences of the native soils and soils with bentonite added. But, preferences for K$^+$ and NH$_4^+$ over Ca^{2+} and K$^+$ over NH$_4^+$ in the native soils and soil–bentonite mixtures were nearly identical, which suggests the presence of similar smectite clays in the soils and bentonite amendments.

The Rothmund–Kornfeld approach, according to Gaines–Thomas convention, yielded good predictions of the exchanger phase composition in a ternary system by use of simple binary-exchange reactions. Although these experiments only addressed Ca^{2+}, K$^+$, and NH$_4^+$, the addition of Na$^+$ to the solution phase, essentially producing a quaternary system, did not hinder the ability of the model to effectively predict equivalent fractions of Ca^{2+}, K$^+$, or NH$_4^+$ on the exchanger phase. Research suggests that combining Mg^{2+} with Ca^{2+} (Feigenbaum et al., 1991) may also be a viable option

for increasing the practicality of the model when investigating environmental issues.

The Rothmund–Kornfeld approach, in conjunction with the knowledge of lagoon-liquor chemistries, may provide a useful tool to aid in the construction of soil liners for animal and municipal waste lagoons (Ham and DeSutter, 2000). This approach allows one to use soil from a proposed construction site and evaluate a soil's ability to selectively adsorb NH_4^+ on its exchange sites. Results from the ternary-prediction experiments indicate that soils from the Great Plains that are used for liner materials could retain about 53 and 23% of the NH_4^+ from swine and cattle lagoons on their exchange sites. Additions of bentonite or zeolite to these soils may not improve the equivalent fraction of NH_4^+ on the exchange sites, when used in conjunction with a swine-waste lagoon. When NH_4^+ concentrations are similar to those found in cattle lagoons, however, the addition of zeolite to soils could help increase the equivalent fraction of NH_4^+ on the exchange sites.

Another useful application of the Rothmund–Kornfeld approach, when used in conjunction with Eq. [1], allows for the prediction of the equivalent depth of soil needed to adsorb 100% of the downward-moving NH_4^+ from waste lagoons. In general, swine lagoons needed a greater equivalent depth of soil, compared with cattle waste lagoons, to adsorb all the NH_4^+. The equivalent depth of soil needed to adsorb 100% of the NH_4^+ from a swine lagoon after 20 yr of operation was as much as 5 m, whereas the soil needed for a cattle lagoon was only as much as about 3 m.

Additional research that should be explored is how effectively the predicted Z_{eq} values compare with actual depths of NH_4^+ movement below swine and cattle lagoons and how downward-moving organic C from animal waste lagoons affects an exchanger's cation selectivity preference and cation exchange capacity. Model validation through the investigation of decommissioned swine and cattle lagoons would allow researchers and regulators to better assess the potential costs for N cleanup and also better identify lagoon construction sites. Increases in CEC are expected with the addition of organic carbon (Parfitt et al., 1995), but some uncertainty in NH_4^+ selectivity still exists when organic C concentrations are increased (Chung and Zasoski, 1994). Another area of exploration is the evaluation of calcareous soils for use as soil liners. Dissolution of carbonates may increase the Ca^{2+} and/or Mg^{2+} content in calcareous soil and, thus, compete with the cations in the lagoon liquor for soil exchange sites and subsequently increase the amount of soil needed to adsorb downward-moving NH_4^+. Prediction of actual concentration profiles of NH_4^+ beneath the lagoon may be possible by incorporating exchange theory with transport theory (Mansell et al., 1988; Mansell et al., 1993; Bond, 1997). Investigating other amendments, such as vermiculite, that may have a greater ability to selectively adsorb NH_4^+ (Evangelou and Lumbanraja, 2002) may help reduce the downward movement of NH_4^+.

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